971. *Boron Hydride Derivatives. Part VI.*[1] *Decaborane Grignard Reagent.*

By I. DUNSTAN, N. J. BLAY, and R. L. WILLIAMS.

The reaction of decaborane, $B_{10}H_{14}$, with methyl- or ethyl-magnesium iodide has been shown to proceed by two routes. The major reaction yields decaboranylmagnesium iodide and methane, and the minor reaction produces 6-methyl- or 6-ethyl-decaborane. Decaboranylmagnesium iodide reacts with triethyloxonium fluoroborate or diethyl sulphate to give 5-ethyldecaborane, but reaction with dimethyl sulphate produces equal amounts of 5- and 6-methyldecaborane. The benzyldecaborane formed by the action of benzyl chloride on decaboranylmagnesium iodide is identified as the 6-substituted derivative.

SIEGEL and his co-workers have recently described [2,3] the preparation of a benzyl-substituted decaborane by allowing decaboranylmagnesium iodide, obtained from decaborane and methylmagnesium iodide, to react with benzyl chloride:

$$B_{10}H_{13}MgI + 2Ph{\cdot}CH_2Cl \longrightarrow B_{10}H_{13}{\cdot}CHPh + CH_2PhI + MgCl_2$$

The ^{11}B nuclear magnetic resonance spectrum of this compound indicated that substitution had not occurred in the apical 2,4-position of decaborane (see I; preceding paper), but no attempt was made to interpret the spectrum more fully. In Parts IV [4] and V [1] the nuclear magnetic resonance spectra of a number of alkylated decaboranes were discussed in detail. The problem of the structure of benzyldecaborane has therefore been re-examined with reference to these substances and extended to include a study of ethyl- and methyl-decaboranes prepared by the action of suitable alkylating agents on decaboranylmagnesium iodide.

Gallaghan and Siegel [5] showed that no reaction occurred between the decaborane Grignard reagent and alkyl chloride, bromide, or iodide, but that trialkyloxonium salts or certain alkyl fluorides gave the corresponding alkyldecaborane in 6—40% yield. It has now been found that dimethyl sulphate, diethyl sulphate, and triethyloxonium fluoroborate react with decaboranylmagnesium iodide to form alkyl derivatives. However, the fluoroborate is less satisfactory than diethyl sulphate for ethylation, since the salt is very hygroscopic and, even when it is used immediately after being prepared, the yield of ethyldecaborane is poor.

EXPERIMENTAL

Reactions of Grignard compounds were carried out in a nitrogen atmosphere.

Decaboranylmagnesium Iodide.—Ethereal methylmagnesium iodide [6] was allowed to react with decaborane which had been recrystallised from n-hexane, to give methane and decaboranylmagnesium iodide as described by Siegel *et al.*[2] The product was obtained as a red, ether-soluble syrup.

Reactions of the Decaborane Grignard Reagent.—(i) *With triethyloxonium fluoroborate.* Triethyloxonium fluoroborate (*ca.* 30 g., 0·16 mole; prepared from boron trifluoride–ether complex and epichlorohydrin [7]) was added to decaboranylmagnesium iodide [*ca.* 10·9 g.; from decaborane (0·04 mole)]. An immediate exothermic reaction occurred and continued for 20 min. The red syrup obtained was stored at room temperature overnight, then ether was removed under diminished pressure and the residue was exhaustively extracted with isopentane

---

[1] Part V, preceding paper.

[2] Siegel, Mack, Lowe, and Gallaghan, *J. Amer. Chem. Soc.*, 1958, **80**, 4523.

[3] Siegel and Mack, *J. Phys. Chem.*, 1959, **63**, 1212.

[4] R. L. Williams, Dunstan, and Blay, *J.*, 1960, 5006.

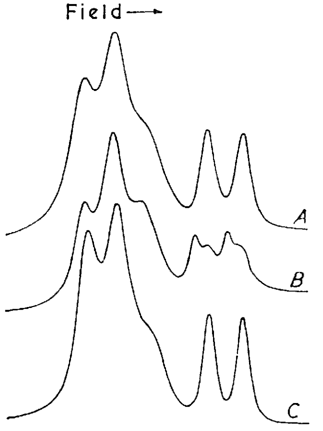
[5] Gallaghan and Siegel, *J. Amer. Chem. Soc.*, 1959, **81**, 504.

[6] Gilman, Zoellner, and Dickey, *J. Amer. Chem. Soc.*, 1929, **51**, 1576.

[7] Meerwein, Battenberg, Gold, Pfeil, and Willfang, *J. prakt. Chem.*, 1939, **154**, 83.

(150 c.c.). Removal of solvent from the extract yielded a red liquid mixture (5·33 g.) of decaborane and its alkyl derivatives which were separated by distillation in an evaporative still into decaborane (1·10 g.) and a colourless liquid (1·093 g.). The latter was shown by gas chromatography to consist of decaborane (30·3%) and 6-methyl- (10·8%) and 5-ethyl-decaborane (58·9%); the yield of 5-ethyldecaborane, based on decaborane converted, was 14·6%. 5-*Ethyldecaborane* had m. p. 1—2° (Found: B, 68·7; C, 16·3%; equiv., 153·5. $B_{10}H_{13}C_2H_5$ requires B, 71·9; C, 16·0%; equiv., 150·2), retention volume 1·93.* It is not possible to detect 6-ethyldecaborane by gas chromatography since this has a similar retention volume to that of 5-ethyldecaborane. However, the infrared spectrum was almost identical with that reported [8] for 5-ethyldecaborane except that some minor peaks were missing. Absence of absorption at 873 and 833 cm.$^{-1}$ showed that very little 6-ethyldecaborane was present. Similarly, the absence of splitting or asymmetry in the high-field doublet of the ^{11}B nuclear magnetic resonance spectrum (see Figure) also shows that the amount of 6-ethyldecaborane must be small. 6-Methyldecaborane was not analysed since its infrared spectrum and retention volume were identical with those of 6-methyldecaborane described in Part V.[1] The ^{11}B nuclear magnetic resonance spectrum is shown in the Figure.

(ii) *With diethyl sulphate.* Redistilled diethyl sulphate (18·46 g., 0·12 mole) was added gradually to decaboranylmagnesium iodide [from decaborane (4·88 g., 0·04 mole)] in ether (100 c.c.). An immediate, exothermic reaction led to a heavy yellow precipitate. After 1 hr., ether was removed and the residue heated on the steam-bath (2 hr.), cooled, and exhaustively extracted with isopentane (150 c.c.). Evaporation of the extract under diminished pressure gave a yellow liquid (7·63 g.) which gas chromatography showed to consist of solvent (including diethyl sulphate) (56·5%), decaborane (12·7%), 6-methyl- (4·0%) and 5-ethyl-decaborane (26·9%), with a small amount of diethyldecaborane. The yield of 5-ethyldecaborane based on decaborane converted was 42·7%. The major components had identical retention volumes and infrared spectra with those reported in (i) above.



The ^{11}B *nuclear magnetic resonance spectra of*:
(*A*) 5-$B_{10}H_{13}Et$.
(*B*) 6-$B_{10}H_{13}Me$.
(*C*) 5-$B_{10}H_{13}Me$.

(iii) *With dimethyl sulphate.* Redistilled dimethyl sulphate (15·1 g., 0·12 mole) was added gradually to a stirred solution of decaboranylmonomagnesium iodide [from decaborane (4·88 g., 0·04 mole)] in ether (100 c.c.). A vigorous, exothermic reaction occurred, giving a yellow precipitate. After 2 hr., ether was removed and the residue was worked up as in (ii). The resulting yellow liquid (4·94 g.) was shown by gas chromatography to consist of solvent (including dimethyl sulphate) (32·2%), decaborane (26·8%), 5-methyl- (17·7%) and 6-methyl-decaborane (23·3%); disubstituted derivatives were present in small amounts. 5-*Methyldecaborane* had m. p. 19—21° (Found: H, 11·5; C, 8·9%; equiv., 138·1. $B_{10}H_{13}CH_3$ requires H, 11·8; C, 8·8%; equiv., 135·2), retention volume, 1·04. The ^{11}B nuclear magnetic resonance spectrum (see Figure) is almost identical with that found for the 5-ethyl derivative, in which the collapse of the high-field component of the low-field triplet shows that 5-substitution has taken place.[8] The 6-methyldecaborane was identified by comparison of its retention volume and infrared spectrum with those of an authentic sample.[1]

(iv) *With benzyl chloride.* Redistilled benzyl chloride (12·65 g., 0·10 mole) was added to decaboranylmagnesium iodide [from decaborane (4·88 g., 0·04 mole)] in ether (70 c.c.). There was no apparent reaction. Working-up as in (ii) yielded a dark viscous oil (8·91 g.). This was purified by preparative gas chromatography, followed by recrystallisation from carbon disulphide, to give crystalline benzyldecaborane, whose infrared spectrum was almost identical with that reported by Siegel *et al.*; [2] however, the BH stretching band at 2500 cm.$^{-1}$ was a single sharp peak even under highest resolution, the bands at 1530 and 760 cm.$^{-1}$ reported by Siegel

---

* All retention volumes are measured at 140° and are relative to naphthalene, V_R = 1·00, and decaborane V_R = 0·78.

[8] Blay, J. Williams, and R. L. Williams, *J.*, 1960, 424.

et al. were absent, and there were small differences in intensity in the region around 1100 cm.$^{-1}$ and from 940 to 820 cm.$^{-1}$. These discrepancies could be due to the different state in which the substance was measured, but this is believed to be unlikely in view of the relative insensitivity of the spectra of decaborane derivatives to change of phase or solvent. The yield of benzyldecaborane was very small, owing to thermal decomposition on the gas-chromatographic column, and insufficient material was available to repeat the measurement of its ^{11}B nuclear magnetic resonance spectrum. However, if the reported spectrum [2] is examined, it is possible to make a structural assignment. Siegel *et al.* have already noted that the splitting of the high-field doublet into four components implies that the decaborane nucleus is unsymmetrically substituted in a position other than the 2-position. Only 5- or 6-substitution fulfils this condition; but the spectra of 5-substituted compounds (see Figure and Part II [8]) show no sign of a splitting in the high-field doublet. Moreover, this splitting is found in 6-methyl- and 6-ethyl-decaborane, so the benzyldecaborane must be 6-substituted. This is confirmed by a consideration of the low-field triplet. The appearance of a new peak on the low-field side of this triplet is the result of the partial collapse of the 6(9)-doublet on substitution, in a similar fashion to that already noted.

Reaction of Decaborane with Ethylmagnesium Iodide.—Redistilled dimethyl sulphate (15·1 g., 0·12 mole) was added gradually to a solution of decaboranylmagnesium iodide [from decaborane (4·88 g., 0·04 mole) and 1·03N-ethereal ethylmagnesium iodide (39·2 c.c., 0·04 mole)] in anhydrous ether (100 c.c.) as described in the previous experiment. The product, a mixture of yellow oil and crystals (4·58 g.), was shown by gas chromatography to consist of solvent (including dimethyl sulphate) (6·4%), decaborane (26·0%), two methyldecaboranes (26·0 and 26·0%), and 6-ethyldecaborane (6·3%). Some disubstitution occurred. The combined yield of methyldecaboranes, based on decaborane converted, was 58·0%. The substances were identified by means of their infrared spectra. There was no indication from the spectrum that 5-ethyldecaborane was present in the 6-ethyl compound.

Experimental Methods.—Analytical gas chromatograms were measured with a Griffin and George mark II apparatus at 140°. Two-metre columns packed with Apiezon L grease (20%) on Embacel support (80%) were used with dry hydrogen as carrier gas. Preparative separations were carried out at 140° on a 12 ft. column, 1″ in diameter, packed with the same stationary phase, except for benzyldecaborane when a 3 ft. column was used at 160°.

Infrared spectra were measured for CS_2 and CCl_4 solutions with either a Grubb–Parsons S3A double-beam prism spectrometer or a GS2 double-beam grating spectrometer.

The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates V4310 C spectrometer at 12 Mc./sec. Samples were measured either as liquids or as CS_2 solutions in 5 mm. diameter tubes.

Equivalent weights were obtained by potentiometric titration of the acetonitrile solution with aqueous alkali.[9,10]

DISCUSSION

The presence of 6-methyldecaborane in the product from decaboranylmagnesium iodide and diethyl sulphate or triethyloxonium fluoroborate can only be explained by the existence of two modes of reaction between decaborane and methylmagnesium iodide, *viz.*:

$$B_{10}H_{14} + CH_3{\cdot}MgI \longrightarrow B_{10}H_{13}MgI + CH_4 \quad \dots\dots\dots \quad (1)$$

$$B_{10}H_{14} + CH_3{\cdot}MgI \longrightarrow B_{10}H_{13}CH_3 + MgHI \quad \dots\dots\dots \quad (2)$$

The proportion of methyl- to ethyl-decaborane in the ethylation products indicates that about 80—90% of the decaborane reacts by mechanism (1) and the remainder by a direct alkylation to give a 6-substituted derivative. The latter reaction is analogous to the nucleophilic substitution of decaborane at the 6-position by methyl- and ethyl-lithium.

In the reaction of decaboranylmagnesium iodide with dimethyl sulphate, both 6- and

---

[9] Atteberry, *J. Phys. Chem.*, 1958, **62**, 1458.

[10] Griffiths and R. L. Williams, *Chem. and Ind.*, 1959, 655.

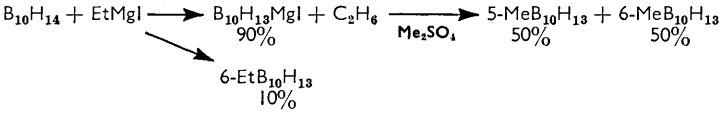
5-methyldecaborane are produced, in the molar ratio of about 5·7 : 4·3. However, about 1·5 mols. of the 6-methyldecaborane arise from the initial reaction (2), so the Grignard compound must react with dimethyl sulphate to yield 5- and 6-methyldecaborane in approximately equimolar amounts:

Relative yields of alkylated decaboranes normalised to a total yield of 10 *moles of product.*

Reaction	5-$MeB_{10}H_{13}$	6-$MeB_{10}H_{13}$	5-$EtB_{10}H_{13}$	6-$EtB_{10}H_{13}$
$B_{10}H_{13}MgI–Et_3O,BF_4$		1·7	8·3	
$B_{10}H_{13}MgI–Et_2SO_4$		1·4	8·6	
$B_{10}H_{13}MgI–Me_2SO_4$	4·3	5·7		
$B_{10}H_{13}MgI$ from $EtMgI–Me_2SO_4$ ...	4·5	4·5		1·0

$$\begin{aligned} B_{10}H_{13}MgI + Me_2SO_4 &\longrightarrow 5\text{-}MeB_{10}H_{13} + MeSO_4{\cdot}MgI\ (50\%) \\ &\longrightarrow 6\text{-}MeB_{10}H_{13} + MeSO_4{\cdot}MgI\ (50\%) \end{aligned}$$

This view is confirmed by examination of the products formed by treating the Grignard compound from decaborane and ethylmagnesium iodide with dimethyl sulphate: 5- and 6-methyldecaborane are formed in approximately equal amounts, together with about 10% of ethyldecaborane. The ethyldecaborane is the 6-substituted derivative and arises from reaction of decaborane with ethylmagnesium iodide in a similar manner to that noted for methylmagnesium iodide:



The reactions of decaboranylmagnesium iodide can be regarded as arising from the partially ionic structure $[B_{10}H_{13}]^{\delta-}MgI^{\delta+}$ and therefore differ from those of decaborane itself. In the case of the latter, there is considerable evidence that the 6-position is the most electropositive in the molecule.[1] However, ionisation of decaborane to yield $B_{10}H_{13}^-$ takes place by abstraction of a bridge proton from between the 5- and the 6-position,[11] thereby enabling electrophilic attack to take place at these positions.

The relative amounts of substitution products when $[B_{10}H_{13}]^{\delta-}MgI^{\delta+}$ reacts seem to depend on the attacking species. Thus, with dimethyl sulphate equal amounts of 5- and 6-methyl derivatives are produced, but with diethyl sulphate the product is predominantly 5-substituted. On the other hand, with benzyl chloride the compound formed is largely 6-benzyldecaborane.

We thank Dr. B. N. Figgis for his co-operation in obtaining the nuclear magnetic resonance spectra, and Mr. F. W. James, of C.D.E.E., Porton, for the analyses.

E.R.D.E., Ministry of Aviation, Waltham Abbey, Essex. [*Received, April 29th,* 1960.]

[11] Lipscomb, *J. Inorg. Nuclear Chem.*, 1959, **11**, 1.